Nanoscale Junctions—A Molecular Foundry User Project

Theory and Experimental Studies of Charge Transport on the Molecular Scale

New computational methods have been developed for the quantitative calculation of the electrical conductance of single molecules. This work, performed by Jeff Neaton in the Molecular Foundry's Theory Facility, with postdoc Su Ying Quek; Foundry users Latha Venkataraman and Mark Hybertsen (Columbia University and Brookhaven National Lab); and collaborator Steven Louie in the Materials Sciences Division, demonstrates that the most advanced theoretical methods are now able to make meaningful comparisons with experiment.

There is considerable current research interest in using organic molecules as components of nanoscale electronic and optoelectronic devices such as solar cells and single molecule transistors. For this field to progress, an understanding of the transport of photons and electrical charge through organic molecular assemblies is crucial. The properties of small structures are often very different from those of bulk materials and both state-of-the-art experimental and theoretical methods are required to evaluate them.

This project focused on the contacts between metals and single organic molecules; many such nanointerfaces will be found in organic-based optoelectronic devices such as hybrid organic-inorganic nanoscale solar cells.

In initial research, a relatively simple system was considered: benzene adsorbed on graphite. The researchers found that the properties of benzene are significantly altered by its interactions with the graphite–for example, its band gap is reduced by 25%. Moreover, they found that the most advanced calculational methods (many-electron perturbation theory within the "GW" approximation), which take into account important electron correlations, were required to discern these effects—specifically conduction levels; use of the simpler "DFT/LDA" method, which treats electron correlations more approximately, did not reveal them.

Later research involved a more complex system–conductance studies of a single molecule of benzenediamine (BDA) between two gold contacts–which can be studied experimentally with scanning-probe tips (NOTE: STM implies something different; a modified STM setup was used) and thus allow a correlation of theory and experiment. The BDA can adsorb to the surface in a variety of ways at different sites on the contacts and 15 such combinations were considered. The electronic structure of the BDA on gold was calculated and the single-molecule conductance for a given contact geometry was predicted using quantum mechanical transport calculations. These theoretical predictions were then compared to an experimental dataset of 59,000 experimental values obtained using scanning-probe tips. Analysis of the experimental data revealed that the 15 different modes of binding all had conductances within a relatively narrow statistical spread (half width) of about 50% of the average value. The spread of the calculated conductances for the 15 different geometries was about 30% of the average value, in good agreement with experiment. The relative insensitivity of the conductance to the contact geometry was attributed to the flexibility of the amine to gold bonding. In addition, building on the earlier calculations of benzene on graphite, the group developed and applied a model GW correction to the DFT results thataccurately account for specific electron correlation effects that affect molecular level alignment in the junction. Their new approach resulted in a predicted average value of the BDA conductance in excellent agreement with the experiments. .

This understanding has led to new methods that can be used to understand, identify, and design optimal metal-molecule contacts in organic optoelectronic devices, e.g. solar cells that will result in more efficient charge injection or collection.

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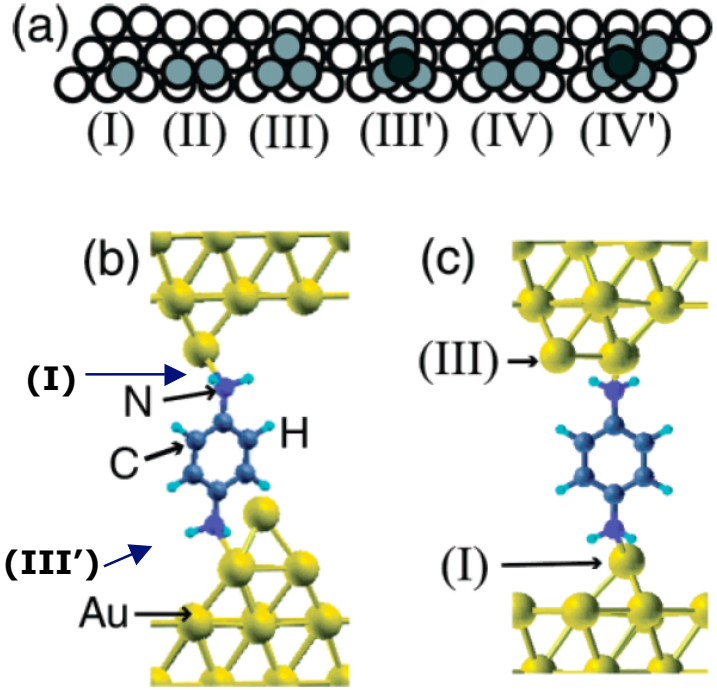
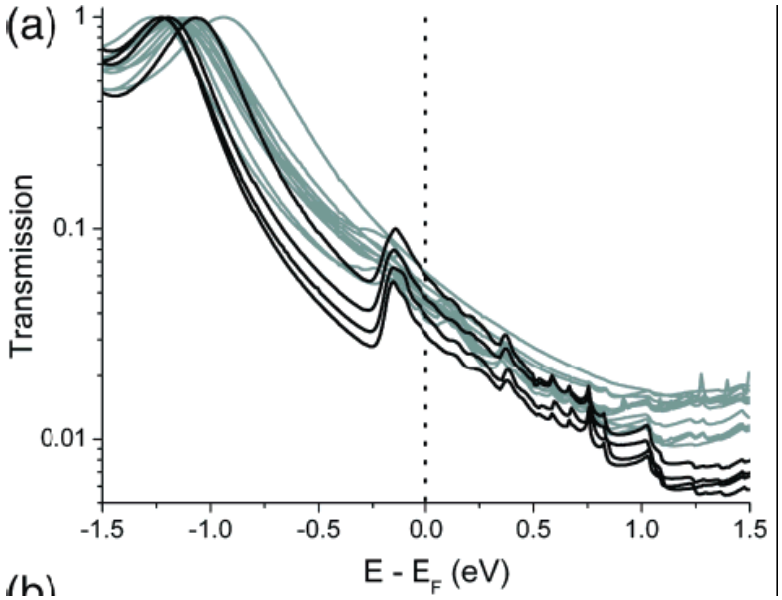


Contact geometries for blue bezenediamine (BDA, blue) between atomic-scale gold electrodes. (a) top view of differing degrees of coordination (I-IV') between the BDA and the gold. For example configuration I bonds through a single H atom on the amine, II bonds with 2 H atoms, etc. (b) shows a (I,III`) "side junction" in which one amine group is bonded to an adatom of gold (I) and the other to an atom at the base of a pyramid (III'). (c) shows a (III, I) junction.



Calculated single molecule conductance data (transmission though the molecule as a function of electron energy relative to a reference value (dashed line) for the 15 different contact geometries considered. Analysis of these curves predicts an average conductance with a spread of +/-30%, in good agreement with experimental measurements of thousands of single molecules junctions which found a spread of 50%.